RELATION BETWEEN ADHESION LOSS AND WATER AT THE POLYMER/SUBSTRATE INTERFACE

Tinh Nguyen, Eric Byrd, David Alsheh, and Dale Bentz

National Institute of Standards and Technology
Gaithersburg, MD 20878

INTRODUCTION

The buildup of water many monolayers thick at the coating/substrate interface is the major cause of adhesion loss when an organic-coated substrate is exposed to water or high relative humidities [1,2]. Until now, it has not been possible to correlate the buildup of the interfacial water layer with adhesion loss because there has been no method available to quantify the water layer at the coating/substrate interface or the adhesion loss of coated substrates. In this study, the thickness of the interfacial water layer and the adhesion loss of several organic film/substrate systems exposed to water were measured and analyzed to establish the correlation between water at the interface and the adhesion loss of organic-coated materials.

EXPERIMENTAL SECTION

Specimen Preparation

For measuring water at the coating/substrate interface, specimens of solvent-free and water-reducible epoxy coatings on untreated and silane-treated 50x10x3mm Si prisms and of asphalts on untreated 50x10x3mm Si prisms were prepared. For measuring adhesion loss, untreated and silane-treated, 100 mm-diameter Si wafers were coated with the epoxy coatings while the asphalts were applied on untreated granite plates. Complete descriptions of solvent-free epoxy, water-reducible epoxy, and asphalts are given in References 3, 4, and 5. Si wafers and prisms were cleaned with acetone followed by methanol, and dried with hot air before use. The surfaces of these Si substrates had an SiO_2 layer about 2.5 nm thick (as measured by an ellipsometer). Under the conditions used in this study (24°C and 45% relative humidity), these surfaces are expected to be covered with hydroxyl groups [6]. The SiO_2-covered Si prisms and wafers are referred to as Si substrates. Silane-treated substrates were prepared by immersing cleaned Si prisms and wafers for 30 minutes in an acidified (pH=4) water solution containing 0.1% aminoethylaminopropyltrimethoxysilane. The treated substrates were dried for 10 minutes at 110°C before applying the organic coatings. Epoxy coatings were applied on Si prisms and wafers using the drawdown technique, similar to that described in Reference 3. The thickness of the solvent-free epoxy coating was in the 130-150 μm range and that of the water-reducible epoxy was in the 120-135μm range. Specimen preparations of asphalts on Si prisms and granite plates are given in References 5 and 7, respectively.

Measurement of Adhesion Loss and Water at the Interface

The specimen configuration and the FTIR-multiple internal reflection (FTIR-MIR) procedure used for determining the amount and thickness of the water layer at the coating/substrate interface are described in Reference 3. The measurements of the adhesion loss of epoxy coatings on Si wafers as a function of exposure in water were conducted using a wet peel adhesion method presented in Reference 8. Twelve specimens on two wafers were tested and the results averaged. The adhesion loss of asphalts on a granite substrate was measured

Proceedings of the Adhesion Society Meeting, February 1995, Hilton Head Island, SC

using a pneumatic pull-off adhesion tester combined with a porous stub, as described in Reference 7. Here, the results were the average of six measurements.

RESULTS AND DISCUSSION

Figure 1 presents the results on the mass and thickness of the water layer at the coating/substrate interface as function of exposure time in water for solvent-free (1a) and water-reducible (1b) epoxy coatings on untreated and silane-treated Si substrates and for asphalts (1c) on untreated Si substrates. Essentially, no water entered the interface of the solvent-free epoxy/silane-treated substrate specimens, but about 10 monolayers (one monolayer of water is approximately 0.3nm thick) have gathered at the interface of the untreated substrates.

For the water-reducible epoxy (Figure 1b), substantial water built up at the interface for both silane-treated and untreated specimens after a short exposure time. Indeed, silane treatment of the substrate surface did not appear to reduce the uptake of interfacial water for the water-reducible epoxy. Figures 1a and 1b also show that much more water has accumulated at the interface of the water-reducible epoxy specimens than that of the solvent-free epoxy specimens. For asphalt systems, the quantity of water at the interface for specimen AAD was substantially greater than that of specimens AAM and AAG.

Figure 2 gives the results on the adhesion loss as a function of time exposed to distilled water for the same coatings on Si wafers and asphalts on a granite substrate. Silane treatment had little effect on the adhesion loss of the water-reducible epoxy but greatly reduced the adhesion loss of the solvent-free epoxy specimens. Further, the water-reducible epoxy specimens lost most of their adhesion at much shorter time than solvent-free epoxy ones. For asphalt systems, specimens AAD and AAG lost their adhesion much faster than specimen AAM.

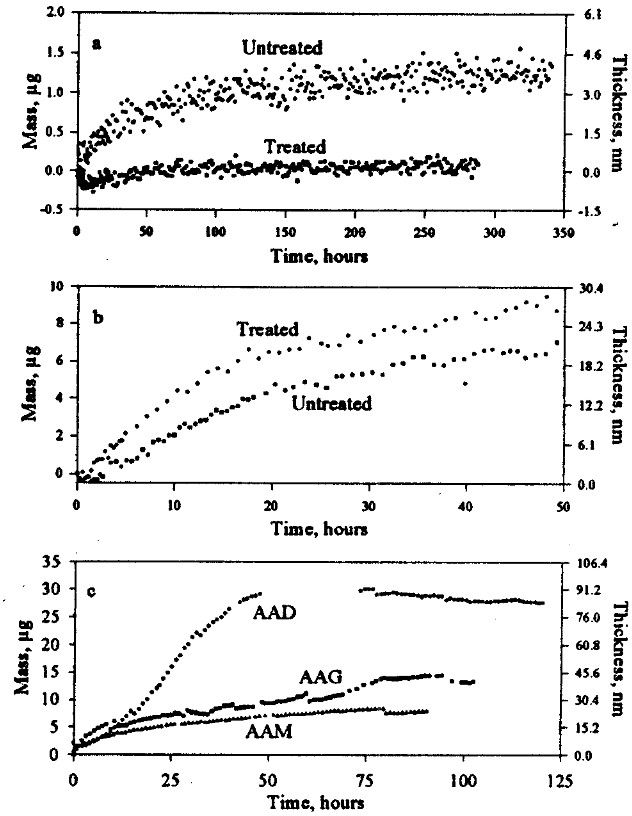

Figure 1. Amount and thickness of the water layer at the coating/Si substrate interface: a) solvent-free epoxy, b) water-reducible epoxy, and c) asphalts.

Except for the water-reducible epoxy specimens that need further investigation, the results presented here indicate that larger amounts of water at the coating/substrate interface generally correspond with greater adhesion loss. Additional data and further analysis are needed to determine more precisely the range of the amount of water at the interface corresponding with the range of the adhesion loss for a variety of coating systems. Once this kind of relationship is well established, the FTIR-MIR technique could be used for studying the adhesion loss at the molecular level.

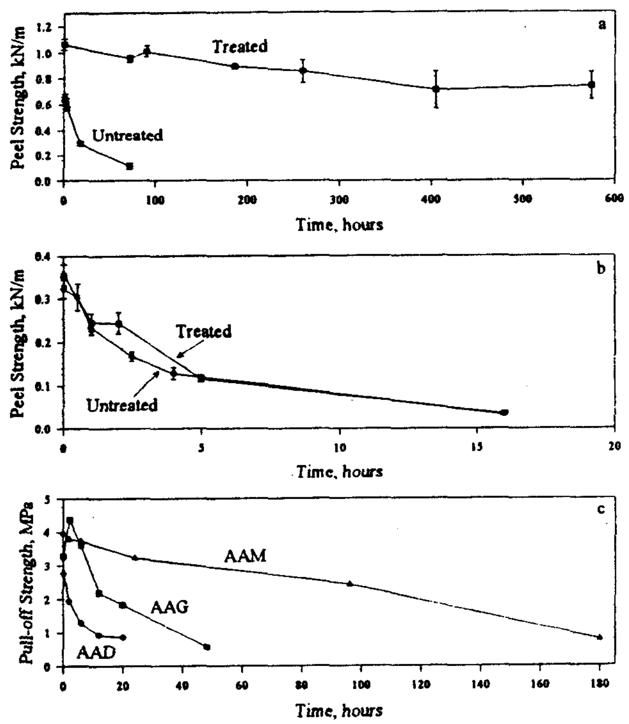

Figure 2. Adhesion loss of coated substrates in water: a) solvent-free epoxy/Si wafer, b)water-reducible epoxy/Si wafer, and c) asphalt/granite.

SUMMARY AND CONCLUSIONS

The buildup of a water layer many monolayers thick at the coating/substrate interface is the major cause of adhesion loss when an organic-coated substrate is exposed to water or high relative humidities. This study investigated the relationship between the adhesion loss and the amount of water accumulated at the interface. Except for the water-reducible coating system, there was, in general, a correlation between the amount of water at the coating/substrate interface and the adhesion loss of an organic coating.

ACKNOWLEDGMENTS

This work is supported in part by the Transportation Research Board, National Academy of Science. We thank Dr. Robert Brady of Naval Research Laboratory for providing the water-reducible epoxy coating.

REFERENCES

1. H. Leidheiser and W. Funke, *J. Oil & Color Chemists' Assoc.*, **70**, 121(1987).
2. D.R. Lefebre, K.M. Takahashi, A.J. Muller, and V.R. Raju, *J. Adhesion Sci. Technol.*, **5**, 204(1991).
3. T. Nguyen, D. Bentz, and W.E. Byrd, *J. Coatings Technol.*, **66**, 39 (1994).
4. T. Nguyen, D. Bentz, and W.E. Byrd, *J. Coatings Technol.*, in press.
5. T. Nguyen, E. Byrd and D. Bentz, National Institute of Standards and Technology Internal Report NISTIR 4783, March, 1992.
6. T. Nguyen, E. Byrd, and D. Bentz, *J. Adhesion*, **48**,169(1995).
7. T. Nguyen, E. Byrd, and J. Seiler, National Research Council NCHRP-IDEA Annual Progress Report 1, Dec. 1994, p.18.
8. D. Alsheh, T. Nguyen, and J.W. Martin, Proceedings, Adhesion Society Conference, February, 1994, p. 209.